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ABSTRACT: This study evaluated the contribution of oily and particulate soil residue to pesticide residue removal. 100% cotton and 65% polyester/35% cotton, were artificially soiled with a standard soil. The fabrics were laundered with the same substrate fabric without soil. Initial methyl parathion contamination was not dependent on the soil level or fiber content of the fabric. Residues remaining after laundering were affected by soiling level. Pesticide residues were greater when the fabric had a heavy soil build-up even though the initial contamination had been lower. Based on these findings, protective apparel should be kept as clean as possible, with daily laundering, for the presence of soil residue affected decontamination of the fabrics.

KEY WORDS: protective clothing, pesticide residue, oily soil, particulate soil, laundering procedures

Accidental spills of pesticide mixtures may occur more frequently during loading, mixing and application activities. Contaminated clothing can act as an occlusive dressing, thus prolonging dermal exposure. Lavy *et al.* [1] have reported symptoms of pesticide intoxication among workers whose clothing was obviously soiled with pesticides. Recent research has addressed issues of sustained risk of pesticide residues in protective apparel and how to remove those residues through effective refurbishment procedures.

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Work to date has examined the problem of 'invisible soil' or pesticide residues remaining in protective work clothing. Most work published to date has evaluated the absorption and after-decontamination retention of pesticide residues on unused (new) fabric. Fabric that is used by pesticide handlers, mixers and applicators may be soiled by particulate soils and/or by oily soils associated with equipment operation and other procedures. This study evaluates the contribution of this pre-existing soil to pesticide contamination and residue removal mechanisms to extend current recommendations for effective refurbishment procedures of protective systems.

The extent of soil removal is affected by the substrate, soil, cleaning method, and interactions of all three. Soils can penetrate the interstitial systems of fabric [2,3]. Since the surface tension of aqueous soils is relatively high, water based soils are usually confined to the surface of a fiber [4]. In contrast, oily soils have significantly lower surface tensions and can penetrate fibers more readily [5]. This penetration is increased by mechanical action such as rubbing and by capillary forces which promote wicking [2].

Laundering recommendations have been published for minimizing direct and indirect pesticide exposure to workers and family members through appropriate laundering procedures. With few exceptions [6-8] laboratory laundering has been used to duplicate the home laundering procedures, and the fabrics studied have been unused or "new" fabrics. During use and subsequent refurbishment, soil residues or changes in fibers due to soil build up can alter responsiveness to soil removal. Oily soiling or particulate soils can be factors that change a fabric's propensity to soiling and responsiveness to refurbishment. Obendorf and Klemash [5] observed large amounts of residual triolein in the interfiber capillaries within the yarns. Cotton fibers also entrapped oil in the crenulations and in the lumen. No triolein was seen in the interior region of polyester fibers, but there were large quantities of residual oil on the fiber surfaces.

The nonpolar fraction components of sebum (body oils), tristearin and triolein, are best removed at a low washing temperature [9]; however, in a mixture of long chain and short chain oily soils, the lower temperature removes the shorter chain hydrocarbons but leaves the long chain hydrocarbons which then polymerize [2]. Unsaturated oily soils may chemically interact with fibers through the aging process making old oily soils difficult to remove. Polymerized oily soils are more difficult to remove [2], and they exhibit a sticky nature which attracts and traps particulate soils [10]. Electron photomicrographs reveal the distribution of particulate soils as concentrated on the filaments of polyester, at the exposed surface of the yarn, and surrounding the fiber in sheath-like form. The

particulate soils do not appear to adhere to the cotton or polyester, but rather to the organic film (oily soils) which coated the fibers [11]. If deposits of oily soils could be prevented, or if a wash process could be devised which would completely remove the oily constituent, the other constituents of soil on textiles could be avoided or removed [11].

Obendorf and colleagues [3,14,15] employed microanalysis techniques to study location of malathion and methyl parathion in fibers and fabrics. Distributions of malathion and methyl parathion were similar, with high concentrations present on the surface of both polyester and cotton fibers and in the cotton lumen. Laundering removed 60-70% of pesticide by cleaning the surface of the fiber, but had little effect on the concentration of pesticide in the cotton lumen. Laundering removed more malathion than methyl parathion from the surfaces of the polyester fiber.

The effect of detergent type on oily soils, including pesticides, has been studied. In the only study reported about the interaction of soil residue and pesticide in fabrics, Laughlin and Gold [13] evaluated whether the oily soil (synthetic sebum and vegetable oil) residues in fabric specimens prior to contamination with pesticide contributed to pesticide absorption and retention. Fabrics of 50/50 cotton/polyester and 100% cotton with two finishes, unfinished and fluorocarbon, with synthetic sebum or vegetable oil, were laundered with and without a prewash product and then contaminated with 1.25% active ingredient (AI) methyl parathion in an emulsifiable concentrate formulation. Residues were always lower when the prewash product had been used, but the combination was not as effective on the all cotton fabric as it was on the cotton/polyester blend fabric. When oily soil had been applied over unlaundered contaminate, more residue was removed in subsequent laundering. But, if oily soil was present before contamination, methyl parathion removal during laundering was less complete.

Obendorf and Klemash [5] evaluated the use of a prewash product that contained an organic solvent on residual triolein. The prewash product significantly reduced the amount of oily soil in the lumen of the cotton fiber and removed it completely from the interfiber capillaries. Keaschall [13] found that use of a prewash product on pesticide contaminated fabrics significantly reduced the amount of residue remaining. Laughlin and Gold [13] consistently used a prewash product in their study.

Obendorf and Klemash [5] found no differences in the amount of residue triolein between fabrics laundered with an unbuilt HDL detergent and with a powdered detergent with carbonate and zeolite builders. Differences were observed between the two detergent types in the location of oily soil residues after laundering. The powdered detergent cleaned

the surfaces of the polyester and cotton fibers more effectively than did the HDL; whereas the HDL detergent cleaned the interfiber capillaries more efficiently than did the powdered detergent.

Laughlin *et al.* [16] recommend use of a heavy duty liquid (HDL) detergent for laundering pesticide contaminated clothing. Hild *et al.* [17] reported that a HDL detergent and a phosphate powdered detergent are equally effective when laundering with a pre-wash product. The additional dose of surfactant in the prewash products supplemented surfactants in detergents. These researchers recommend increasing the amount of detergent, using more than that specified on the detergent package as a means to reducing interfacial tensions, thus reducing the time required for induction and diffusion of the wash liquor into the fabric. Mineral content of water effects detergent solution. Laughlin and Gold [18] recommend supplementing phosphate detergent with additional amounts of detergent or with a pre-wash product, especially as level of water hardness increases.

Based on these data Laughlin and Gold [13] recommended that applicator clothing, especially of all cotton fiber content, be kept as clean as possible relative to oily soils such as body oils, machinery oils, or oily food stuffs. Residuals of oily soils in fabrics complicate residue removal. The results of that study illustrate the importance of removing all previous soil, particularly oily soil, from apparel fabrics prior to exposure to pesticide to minimize residue accumulation.

Obendorf and Klemash [5] reported that increased concentrations of detergent significantly lowered the amount of residual triolein remaining in laundered fabrics. However, if too much detergent is used in the wash liquor, the suds act as cushions, and thus may inhibit the penetration of the wash liquor into the fabric substrate [17]. This is especially true in front loading washing machines where agitation is through the tumbling action of the revolving washer drum.

Work to date on laundering pesticide contaminated apparel fabric has established the relationship between emulsifiable concentrate formulations and oily soils, and between wettable powders and particulate soil. Study of the relationship between oil soils (such as sebum, or vegetable oils) and particulate soils on pesticide absorption and retention following refurbishment was needed, since research in the literature has not yet considered these factors simultaneously.

PURPOSE

This study was undertaken to determine whether the

residues of oily soils and particulate soils in fabric for protective apparel affect pesticide absorption and residue retention after subsequent laundering. Of specific interest was the soil transfer phenomenon, that is, would a heavily soiled fabric (oily and particulate soils) laundered with an unsoiled fabric, transfer enough soil to the "clean" fabric to assist in or interfere with pesticide absorption and residue retention.

Research Design

The research design included two dependent variables, residue in the fabric and whiteness of fabric as an indicator of relative presence or absence of soil. Prior to exposure to methyl parathion, heavily soiled fabric was laundered to model a soil level similar to that found in soiled and laundered clothing of agricultural workers. The laundry load included a "clean" (never soiled) fabric to evaluate redeposition of soil and the contribution of a "light" soil residue on pesticide absorption and retention.

The fabrics were TestFabrics WFK 10A-100% cotton and WFK 20A-65% polyester/35% cotton. The fabrics were artificially soiled with a soil composed of 84% clay, 8% lampblack, 4% black iron oxide, and 2% yellow iron oxide in the first precision spray nozzle and 3.4% lanolin dissolved in carbon tetrachloride and salt solution in the second spray nozzle (Waescherei Forschungs Institute's standard soil). The same fabrics without the artificial soil, WFK 10C-100% cotton and WFK 20C-65% polyester/35% cotton, were used for the "clean" fabric to evaluate redeposition. Prior to contamination, lengths of WFK 10A (100% cotton with standard soil) were laundered with WFK 10C (same fabric, without standard soil) and lengths of WFK 20A (65% polyester, 35% cotton with standard soil) were laundered with WFK 20C (same fabric, without standard soil). An automatic home washing machine was used, with a standard four pound load, "tap" water (171 ppm dissolved solids) at 50°C [American Association of Textile Chemists and Colorists (AATCC) Test Method for Dimensional Change in Automatic Home Laundering of Woven and Knit Fabrics (135-1978, Revised 1982)]. A powdered phosphate (anionic) detergent (PHOS), and a heavy duty liquid (nonionic and anionic) detergent (HDL) were used in two separate procedures for the laundering-before-contamination pretreatment. Fabrics of the two fiber contents were laundered separately using each of the laundry detergents (HDL or PHOS), resulting in four separate launderings and fabrics with eight pre-contamination treatments.

The random complete block research design (2 x 2 x 2) included: two detergents (heavy duty liquid detergent (HDL) and phosphate powdered detergent (PHOS)); two levels of soiling (original soil and redeposition during laundering); and the two fiber contents. Two response variables were measured: color change as an indicator of soil level, and

pesticide residue remaining after laundering. After-laundering pesticide residue was determined for the original soiled (but laundered before contamination) specimens and the same substrate fabric without soil, hereafter called redeposition specimen.

Before randoming sampling the eight fabric lengths, the outer 10% of the fabric width was removed to ensure consistency of the warp yarns [American Standards for Testing Materials (1986) Test for Breaking Load and Elongation of Textile Fabrics (D-1982-64, R-15)]. Fabrics were cut to 8 x 8 cm swatches by following a cutting diagram, with random assignment to treatments.

Measuring Soil in Fabric

Effectiveness of laundering in removal of standard soil and soil redeposition onto "clean" fabrics were determined by color reflectance measurement [AATCC Test Method 153-1985 Color Measurement of Textiles: Instrumental]. Reflectance measurements were made on the four orientations of each specimen. A Hunter Lab Scan II Color Difference meter was used for all reflectance measurements. Reflectance values were taken from all specimens before laundering, and after laundering as well as the unsoiled specimen that had been laundered with the originally soiled specimen.

Fabric Contamination

Each specimen was initially contaminated (spiked) with a 1.25% solution of methyl parathion [(0,0-dimethyl) o,p-nitrophenyl phosphorothioate] (MeP) emulsifiable concentrate formulation. A magnetic stirrer provided uniform agitation of the pesticide solution during the contamination process.

Specimens were placed on a raised needle bed surface to minimize contact points during contamination. A Microlab P programmable micropipette, held in a padded ring stand to maintain an equal distance of 5 cm between pipette tip and specimen, was used to dispense 0.20 ml of MeP onto the fabric surface. Specimens were air dried four to six hours.

Prewash Treatment

A prewash product, Spray-n-Wash®,[2] manufactured by Texize, was applied to the MeP spiked area of the contaminated fabric specimens prior to laundering. The procedures used for contamination were followed to dispense 0.25 ml of the prewash product onto the fabric specimen surface. This volume was selected to thoroughly saturate the spiked area.

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[2]Use of brand names does not imply endorsement of product.

General Procedures for Laundering

A modification of the procedures outlined in AATCC Standard Test Method for Washing, Domestic, and Laundering, Commercial; Accelerated (61-1980) was used for a single laundering of specimens. The wash liquor consisted of 150 ml of a 0.13% solution of an unbuilt nonionic heavy duty liquid detergent (HDL), Dynamo®,[2] manufactured by Colgate Palmolive Co, or 150 ml of a 0.20% solution of powdered phosphate (PHOS) detergent (Cheer®)[2] manufactured by Proctor and Gamble Corporation. Water used throughout the experiment was distilled and deionized. The wash liquor was placed in round stainless steel canisters, 7.6 cm in diameter and 12.4 cm tall, with 25 steel balls. The canisters were sealed with caps lined with rubber gaskets and teflon liners. Following a 10 minute preheat cycle, specimens were laundered for 12 minutes in an AATCC Atlas Launder-Ometer model LEF at 60°C. The wash liquor was decanted and specimens were subjected to both a 5 minute and a 3 minute rinse cycle of 150 ml distilled water at 40°C. At the completion of the laundering cycles, specimens were air dried.

Extraction Procedures

To extract the pesticide remaining in specimens after laundering treatment, individual fabric swatches were placed in 476 ml specimen bottles with teflon lined caps. Specimens were shaken for 30 minutes in an aliquot of 100 ml of hexane on a mechanical shaker at 120 cpm. The extract was decanted and replaced by a second 100 ml and specimens were subjected to an additional 30 minute cycle. After the two cycles, the fabrics were removed, and the extracts combined.

Gas Chromatography Procedures

Depending on MeP concentration, the extracts were either concentrated on a rotary vacuum evaporator or diluted with additional hexane for analysis on a gas chromatograph. Analysis of the pesticide residue remaining after treatment was obtained with double injections on a Varian Vista Series 3400 gas chromatograph with dedicated microprocessor and electron capture detector. The separation column was 2-m x 2-mm glass packed with 10% OV-101 Chromosorb W with a nitrogen flow of 40 ml per minute. Operating temperatures were 220°C, 250°C, and 325°C for column oven, injector, and detector, respectively. The External Standard Approach was the method used for calibration.

Statistical Analysis

MeP residues were expressed as $\mu g/cm^2$ remaining and as a percentage of the initial contamination for statistical analysis. All work was replicated a minimum of three times. Using recovery rates, an arc sine conversion of percentages

of residue remaining after laundering was performed. Statistical differences were established by the General Linear Model (GLM) with means separated by the Least Significant Means test at $p \leq 0.05$.

Controls

To determine the amount of pesticide initially absorbed by each finish at contamination, specimens of each finish were contaminated and analyzed unlaundered for each replication of the experiment. Pesticide solution was also placed in glass to determine recovery rates.

FINDINGS AND DISCUSSION

A continuing dilemma in the issue of pesticide protective apparel are fabrics that look clean while still carrying pesticide residue after laundering. In a twist on this phenomena, this study uses objective measures of relative cleanliness of "used" fabric to establish the contribution of soiling to pesticide residue absorption and retention. Color change determined by reflectance measurements (ΔE) were used to determine soil residue in fabrics. Inferences were drawn about the association between the soil residues in fabric and the pesticide residue in fabric. The research sought to answer three questions, and the findings are presented in the framework of these questions: 1) Does soil residue remaining after laundering affect pesticide absorption and retention; 2) Does redeposition of soil in laundering affect pesticide absorption and retention; and 3) Does a difference in soil residue level make a difference in pesticide absorption and retention?

Soil Residue in Laundered Heavily Soiled Fabric

The Originally Soiled Specimens (OSS) were laundered to remove the soil. To determine if laundering was effective, determinations of color change were made between the OSS and a clean, but individually laundered specimen. The "control" or working standard was laundered so that any effects of detergents, including whiteners and/or optical brightness would be consistent.

Laundering the OSS did remove great quantities of soil, but the soil residue in the fabric was pronounced so that there was an obvious change in reflectance (ΔE) of the "laundered OSS" (Table 1). Interaction of fiber content and detergent type ($F(1)=101.05$, $p \leq 0.02$) affected main effects. A main effect of fiber content was present ($F(1)=296.61$, $p \leq 0.05$) with more soil residue on the polyester/cotton fabric ($\Delta E=16.23$) than the cotton fabric ($\Delta E=6.35$). Detergent type was a significant main effect ($F(1)=124.46$, $p \leq 0.01$). All color change means were significantly different from no change. The interaction was

of fiber content and detergent type, with ΔE means of 6.03 and 6.67 for cotton laundered in HDL and PHOS, respectively, and ΔE means of 10.15 and 22.47 for polyester/cotton laundered in HDL and PHOS, respectively. There was no significant difference between the two color difference values for cotton, but cotton was different from cotton/polyester and the two color difference values for the blend were significantly different. Therefore, based on these data, soil was left in the fabric which could affect absorption and retention of methyl parathion, and the soiling level was much greater in the polyester/cotton than in the cotton. The PHOS detergent had been less effective at removal of the oily and particulate soil combination than had the HDL detergent.

TABLE 1--Color reflectance measurement of color change (ΔE) in originally soiled specimens and redeposition specimens after laundering.

	ΔE	
Specimens	Originally soiled specimens	Redeposition specimens
Cotton		
HDL[a]	6.03	3.64
PHOS[b]	6.67	4.07
Polyester/ Cotton	10.15	0.47
HDL	22.47	12.64
PHOS		

[a]HDL=Heavy Duty Liquid Detergent.
[b]PHOS=Phosphate Powdered Detergent.

Soil Gain in Soil Redeposition Fabrics

"Clean" fabric specimens were laundered with the OSS to determine whether soil redeposition occurred. Soil redeposition or soil gain on clean specimen would manifest as color gain over the standard or "white" fabrics. In this study, the transfer or redeposition specimens (RS) had significant color, or soil gain, with an interaction of fiber content and detergent type ($F(1)=60.55$, $p \leq 0.01$) and main effects of fiber content ($F(1)=12.49$, $p \leq 0.01$) and detergent type ($F(1)=68.45$, $p \leq 0.01$). The interaction showed no differences for cotton between the HDL detergent and the PHOS detergent (ΔE=3.64 and 4.07, respectively), but ΔE's for the polyester/cotton blend were detergent specific. Based on these data, the greater propensity to redeposit soil on the polyester/cotton blend may be a factor of note for methyl parathion absorption and retention.

Soil Levels in Originally Soiled Specimens vs Redeposition Specimen

The possibility that soil level could affect pesticide absorption and retention was important. To answer the question whether difference in soil levels were present between laundered OSS and the soil gained by the RS, color reflectance comparisons (ΔE) were contrasted.

Hypothetically, this comparison was of a "white" (OSS, specimen after laundering) with a "white" (RS, redeposition or transfer specimen); in a practical sense, soil residue and redeposited soil were the color agents present after laundering (Table 2). Analysis of these data resulted in main effects attributable to fiber content (F=12.49, df=1,3, $p \leq 0.05$) and detergent type (F=68.45, df=1,3, $p \leq 0.05$) as well as an interaction of fiber content and detergent type (F=60.55, df=1,3, $p \leq 0.05$). Specimens of the two fiber contents were more similar (cotton=ΔE 3.88, polyester/cotton=ΔE 6.56) than were specimens laundered in the two detergent types (HDL=ΔE 2.08, PHOS=ΔE 8.36). The response for the two sets of cotton specimens laundered in HDL to be very similar in reflectance (ΔE=3.64) while the two sets of cotton/polyester specimens laundered in the PHOS were quite different (ΔE=12.64).

TABLE 2--Color reflectance measurement (ΔE) of redeposition specimens compared to after laundering originally soiled specimen (soil level).

	ΔE[c]
Cotton	
HDL[a]	18.62
PHOS[b]	18.03
Polyester/Cotton	
HDL	5.05
PHOS	5.74

[a]HDL=Heavy Duty Liquid Detergent.
[b]PHOS=Phosphate Powdered Detergent.
[c]OSS as Standard: L*=72.85, a*=-0.26, b*=1.56.

With the reflectance measurements as indicator of level of soiling established, the focus of the project shifted to the removal of pesticide residue from fabrics.

Initial Contamination Levels

The level of contamination at spiking was 18.82 ± 4.25 $\mu g/cm^2$ on the cotton control specimens and 16.67 ± 9.03 $\mu g/cm^2$ on the cotton/polyester control specimens. There were no statistical differences in initial contamination due to fiber content (F=1.48, df=1,35, n.s.). The Originally Soiled Specimens (OSS), laundered before spiking, held 17.25

± 8.58 $\mu g/cm^2$ of MeP, while the "clean" or working standard specimens, laundered before spiking, held 16.33 ± 10.47 $\mu g/cm^2$. There were no statistical differences in initial contamination (F=0.67, df=1,71) due to soil residue level. While no significant difference at initial contamination due to fiber content is in agreement with most previous studies, one hypothesis in this research was that different levels of soil in fabrics (heavy residue of soil contrasted to light soil or redeposition) might affect pesticide absorption at initial contamination. This hypothesis was not supported by these data.

MeP Residue Remaining After Laundering

Laundering removed significant quantities of Methyl Parathion (MeP) (Table 3). Residue remaining after laundering differed significantly with main effects attributable to fiber content and soil history, but not due to detergent type (Table 4 and 5). The laundered OSS (moderate soil) retained 0.77 $\mu g/cm^2$ (5.3%) of initial level of contamination while the redeposition (or transfer) specimen (RS) had residues of 2.69 $\mu g/cm^2$ (15.1%) of initial contamination. Based on these data, oily and particulate soil residues do affect post laundering residue retention. The more heavily the soilings of the fabric, the less pesticide residue is retained after refurbishment, perhaps because refurbishment releases soil residue taking pesticide that is tied-up or bound to the soil.

TABLE 3--Methyl parathion residue remaining in originally soiled specimens and redeposition transfer specimens after laundering.

	$\mu g/cm^2$		%	
	X [a]	s.d.	X [a]	s.d.
Originally Soiled Specimens				
Cotton				
HDL[b]	0.33[j]	±0.46	2.5[j]	±1.9
PHOS[c]	0.71[j]	±0.73	1.5[j]	±1.4
Polyester/Cotton				
HDL	1.20[j]	±0.69	4.2[j]	±2.3
PHOS	1.45[j]	±1.76	5.4[j]	±3.1
Redeposition Specimens				
Cotton				
HDL	1.66[j]	±2.16	8.3[j]	±17.9
PHOS	1.77[j]	±1.52	9.1[j]	±16.8
Polyester/Cotton				
HDL	4.20[k]	±2.77	27.5[k]	±13.5
PHOS	3.31[k]	±1.88	19.9[k]	±11.5

[a]Means with the same superscript letter (j or k) are not statistically different, $p \leq 0.05$.
[b]HDL = Heavy Duty Liquid Detergent.
[c]PHOS = Phosphate Powered Detergent.

TABLE 4--Analysis of variance for amount of MeP residue remaining after laundering originally soiled specimens and redeposition specimens.

Source	df	F	P
Soil history (Soil)	1	5.65	0.02*
Fiber Content (Fiber)	1	3.59	0.05*
Detergent Type (Det)	1	0.02	0.91
Model	7		
Contrast			
Soil x Fiber	1	0.27	0.62
Soil x Detergent Type	1	0.03	0.87
Fiber x Detergent Type	1	0.03	0.87
Soil x Fiber x Detergent Type	1	0.18	0.69

*$p \leq 0.05$

TABLE 5--Analysis of Variance for percentages of MeP residue remaining after laundering originally soiled specimens and redeposition specimens.

Source	df	F	P
Soil history (Soil)	1	5.17	0.02*
Fiber Content (Fiber)	1	4.93	0.04*
Detergent Type (Det)	1	0.51	0.49
Model	15		
Contrast			
Soil x Fiber	1	0.46	0.52
Soil x Detergent Type	1	0.01	0.94
Fiber x Detergent Type	1	0.61	0.46
Soil x Fiber x Detergent Type	1	0.12	0.73

*$p \leq 0.05$

Laughlin and Gold (1990) reported that oily soil residue in fabric lowered initial levels of contamination by "protecting" the fiber from penetration of the pesticide residue. Yet, they reported that pesticide (MeP) residue was more difficult to remove from fabrics unless "vigorous" laundering procedures were employed. The current study did use the pre-wash product, and good residue removal results may be attributable to the additional dosage of surfactant. However, the very high levels of MeP residue in the redeposition or transfer specimen may be due to a function of these same two phenomena working in reverse. The redeposition or transfer specimen did not have the heavy oily soil to impede pesticide penetration, and the laundering procedure transferred soil, including the long chain hydrocarbons and particulate soils which may have entrapped pesticide residues. In this instance, the lower soil level was more problematic because of the nature of the

soil.

After-laundering residues of MeP were significantly greater in the cotton/polyester specimens (2.53 $\mu g/cm^2$, 15.7%) than in the cotton specimen (0.92 $\mu g/cm^2$, 4.6%). It is important to note that there was no significant difference at initial contamination due to fiber content, and these findings of fiber content differences are not supported by findings reported in the literature of previous work where the research was done with "clean" specimens, or fabrics without a "used" condition of soil residue in the fabric.

To explore this further, additional work was done to ascertain whether the OSS and RS working standards exhibited differences at initial contamination due to fiber content. In comparison to the working standards, or the OSS that had been laundered prior to contamination, the cotton OSS absorbed 14.83 $\pm$ 8.76 $\mu g/cm^2$ and the polyester/cotton OSS absorbed 19.71 $\pm$ 7.88 $\mu g/cm^2$ (F=1.66, df=1,17, $p \leq 0.05$). Average amounts of MeP on cotton transfer specimens were 18.82 $\pm$ 14.25 and on polyester/cotton transfer specimens were 16.77 $\pm$ 9.68. These differences were not statistically significant (F=0.62, df=1,35). These data reflect preferential absorption of pesticide onto the polyester/cotton specimens with soil residues; while the cotton specimens with soil residues absorbs less pesticide at initial contamination. These observations are confirmed by the reflectance measurements, with after-laundering soil residue greater in the polyester/cotton blend specimens (ΔE=16.23) than in the cotton specimens (ΔE=6.35).

The impact of lighter soiling loads can be ascertained through the data for the redeposition ("transfer") specimens. The means differed (H_o: t = 0) for polyester/cotton specimens laundered in HDL ($\mu g/cm^2$ = 1.20) and for polyester/cotton blend laundered in PHOS detergent ($\mu g/cm^2$ = 1.45). These redeposition specimens had heavier pesticide residue levels than did the OSS (see Table 3). Although detergent type was not a significant main or interaction effect, PHOS was more effective than HDL when the soil load was heavy.

Fibers, twisted into yarns, and fabricated by weaving should be considered as porous structures open to soil. When the soiling load is very heavy, all the spaces in the fabric structure, the yarn bundle, or the fiber become filled with particulate or oily soil. There are fewer sites for additional soil, in this study, pesticides, to become entrapped or bind. With less penetration of pesticide, the residue is more completely removed in laundering. However, when the fabric is lightly soiled, many soiling sites remain open to accept pesticides. When the pesticide penetrates deeply into the structure of the fabric, the yarn bundle, or the fiber, residue removal is less complete. In this study, the heavily soiled (OSS) and the residue of that heavy soil,

as determined by reflectance measures, limited initial contamination; while the lightly soiled (as determined by reflectance measures) redeposition specimens held pesticide residue more tenaciously.

Based on these data, keeping work clothing as clean as possible is an important part of maximizing pesticide worker protection. The presence of oily and particulate soils in clothing fabric enhances methyl parathion absorption and makes residue removal more problematic. Soil residue loading contributes to pesticide absorption and residue retention, with lighter levels of soil residue contributing to greater after-laundering residue retention than heavier levels of soil residue where a protective layer of oily soil is present. Pesticide of other formulations and classes merit evaluation under this protocol. Specifically, the interaction of pesticide formulation and soil type should be studied.

REFERENCES

[1] Lavy, T.L., Mattie, J.D. and Flynn, R.R., "Field Studies Monitoring Worker Exposure to Pesticides," *Performance of Protective Clothing, ASTM 745*, K.G. Seymour, Ed., American Society for Testing and Materials, Philadelphia, 1986, pp. 136-150.

[2] Bevan, G., "Mechanisms of Soil Textiles," *Textiles*, Vol. 8, No. 3, March 1979, pp. 69-71.

[3] Solbrig, C.M. and Obendorf, S.K., "Distribution of Residual Pesticide Within Textile Structures as Determined by Electron Microscopy," *Textile Research Journal*, Vol. 55, No. 9, September 1985, pp. 540-546.

[4] Wentz, M., Lloyd, A.C. and Watt, A., "Experimental Removal of Stains," *Textile Chemist and Colorist*, Vol. 7, No. 10, October 1975, pp. 179-183.

[5] Obendorf, S.K. and Klemash, N.A., "Electron Microscopical Analysis of Oily Soil Penetration Into Cotton and Polyester/Cotton Fabrics," *Textile Research Journal*, Vol. 52, No. 7, July 1982, pp. 434-442.

[6] Finley, E.L. and Rogillio, J.R.B., "DDT and Methyl Parathion Residues found in Cotton and Cotton-Polyester Fabrics Worn in Cotton Fields," *Bulletin of Environmental Contamination and Toxicology*, Vol. 4, No. 6, June 1969, pp. 343-351.

[7] Lillie, T.H., Livingston, J.M. and Hamilton, M.A., "Recommendations for Selecting and Decontaminating Pesticide Applicator Clothing," *Bulletin of Environmental Contamination and Toxicology*, Vol. 27, No. 6, June 1981, pp. 716-723.

[8] Laughlin, J. and Gold, R.E., "Methyl Parathion Redeposition During Laundering Functionally Finished Apparel Fabrics," *Bulletin of Environmental Contamination and Toxicology*, Vol. 42, No. 5, May 1989, pp. 691-699.

[9] Morris, M.A. and Prato, H.H., "The Effect of Wash Temperatures on Removal of Particulate and Oily Soil from Fabrics of Varying Fiber Content," *Textile Research Journal*, Vol. 52, No. 4, April 1982, pp. 280-286.

[10] Bowers, G.A. and Chantrey, G., "Factors Controlling the Soiling of White Polyester Cotton Fabrics," *Textile Research Journal*, Vol. 39, No. 1, January 1969, pp. 1-11.

[11] Fort, T. Jr., Billica, H.R. and Sloan, C.K., "Studies of Soiling and Detergency Part I: Observations of Naturally Soiled Textile Fibers," *Textile Research Journal*, Vol. 36, No. 1, January 1966, pp. 7-12.

[12] Keaschall, J., Laughlin and Gold, R.E., "Effect of Laundering Procedures on Pesticide Removal Between Classes," *Performance of Protective Clothing, ASTM STP 900*, R.L. Baker and G.C. Coletta, Eds., American Society of Testing and Materials, Philadelphia, 1986, pp. 136-150.

[13] Laughlin, J. and Gold, R.E., "Methyl Parathion Residue Removal from Protective Apparel Fabrics Soiled with Synthetic Sebum or Vegetable Oil," *Archives of Environmental Contamination and Toxicology*, Vol. 19, No. 2, Feb. 1990, pp. 205-213.

[14] Uyenco, E.F.T. and Obendorf, S.K. "Effect of Functional Finishes on Retention of the Pesticide Malathion on Polyester/Cotton Fabrics," *AATCC Book of Papers,* pp. 239-247.

[15] Obendorf, S.K. and Solbrig, C.M., "Distribution of the Organophosphorus Pesticides Malathion and Methyl Parathion on Cotton/Polyester Fabrics After Laundering as Determined by Electron Microscopy," *Performance of Protective Clothing, ASTM STP 900*, R.L. Baker and G.C. Coletta, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 187-292.

[16] Laughlin, J., Easley, C. and Gold, R.E., "Methyl Parathion Residue in Contaminated Fabrics after Laundering," *American Chemical Society Symposium Series*, No. 273, 1985, pp. 177-187.

[17] Hild, D.N., Laughlin, J. and Gold, R.E., "Laundry Parameters as Factors in Lowering Methyl Parathion Residue in Cotton/Polyester Fabrics," *Archives of Environmental Contamination and Toxicology*, Vol. 18, No. 1, Nov. 1989, pp. 908-914.

[18] Laughlin, J. and Gold, R.E., "Levels of Water Hardness, Detergent Type and Prewash Product Use as Factors Affecting Methyl Parathion Removal," *Clothing and Textiles Research Journal*, Vol. 8, No. 2, Summer 1990, pp. 61-67.